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Title: PROCESS FOR THE PRODUCTION OF METHYL OR ETHYL MONO-HALIDE ;

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ABSTRACT:

Alkyl monohalides wherein the alkyl substituent is methyl or ethyl are selectively produced by reacting a halogen with methane or ethane in the absence of a catalyst and at a temperature below 300 DEG C, provided that in the absence of electromagnetic radiation the temperature is greater than the thermal initiation temperature. In a preferred embodiment methyl monochloride is selectively produced by reacting methane with chlorine.

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(54) **Process for the production of methyl or ethyl mono-halide**

(57) Alkyl monohalides wherein the alkyl substituent is methyl or ethyl are selectively produced by reacting a halogen with methane or ethane in the absence of a catalyst and at a temperature below 300°C, provided that in the absence of electromagnetic radiation the temperature is greater than the thermal initiation temperature. In a preferred embodiment methyl monochloride is selectively produced by reacting methane with chlorine.

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SPECIFICATION

Process for the production of an alkyl mono-halide wherein the alkyl substituent is methyl or ethyl

The present invention relates to a process for the production of an alkyl mono-halide wherein the alkyl substituent is methyl or ethyl.

Methyl mono-halides, being functional derivatives of methane, are potentially important intermediates in the production, for example of methanol. Converting methane to methyl mono-halides and thence to methanol offers an alternative to converting it first to synthesis gas (carbon monoxide + hydrogen) and thereafter to methanol. Similarly, ethyl mono-halides, being functional derivatives of ethane, are potentially important intermediates in the production, for example of ethanol. Converting ethane to ethyl mono-halides and thence to ethanol offers an alternative to converting it first to ethylene and thereafter to ethanol. It is known to produce such alkyl mono-halides by reacting methane or ethane with a halogen, but this is conventionally carried out at elevated temperatures at which the selectivity to the desired alkyl mono-halides is low, there being generally formed in addition to the alkyl mono-halide a variety of halogenated alkane derivatives. Thus in the case of chlorine as the halogen for example the reaction is usually carried out at temperatures near 450°C at which temperature in addition to methyl chloride substantial amounts of methylene dichloride, chloroform and carbon tetrachloride are also obtained.

It has now been found unexpectedly that alkyl mono-halides wherein the alkyl substituent is methyl or ethyl can be obtained in high selectivities and with high conversions of alkane or halogen in the absence of a catalyst under relatively mild conditions.

Accordingly, the present invention provides a process for the selective production of an alkyl mono-halide wherein the alkyl substituent is methyl or ethyl which process comprises reacting a halogen with an alkane which is methane or ethane in the absence of a catalyst and at a temperature below 300°C, provided that in the absence of electromagnetic radiation the temperature is greater than the thermal initiation temperature.

Both methane and ethane are abundantly available in hydrocarbon reservoirs. Methane may also be obtained by the biological conversion of organic materials and by the methanation or in-situ gasification of coal. Halogens and in particular chlorine are readily available on an industrial scale. Suitably the halogen may be either chlorine or bromine and is preferably chlorine.

The reaction is carried out in the absence of a catalyst. However, it is preferred to react the halogen with the alkane in the presence of an inert material. The inert material may be any material which does not react in a chemical sense with or remove alkane or halogen from the system. Alternatively, the inert material may be any material which becomes inert after an initial stabilisation period in the presence of the reactant gases. During the stabilisation period reaction between the reactant gases and the material may occur but thereafter the material is essentially chemically inert to the reactants. The presence of an inert material facilitates the transfer of heat during the reaction. Suitable inert materials include glass wool, alumina, silica, clay, porcelain and the internal surface of the vessel in which the reaction is carried out.

Energy is required to effect initiation of the reaction of the alkane with a halogen. Any suitable form of energy may be used but it is preferred to use thermal energy, electromagnetic radiation energy or chemical energy. Any combination of these forms of energy may be used if so desired. The nature and quantity of energy required will depend on the particular halogen employed. In the case of chlorine for example, the reaction with methane may suitably be initiated either by visible light, or in the dark by thermal energy at temperatures above about 180°C. At lower temperatures, in the absence of electromagnetic radiation, thermal initiation of the reaction does not occur to any appreciable extent. It is believed that the energy input is required to dissociate the halogen molecule into free radicals which are active in the reaction steps, though it is not intended to be bound in any way by this theory.

In order to sustain a continuous reaction or high yields in a batch process further quantities of initiation energy must be supplied. The additional energy may be supplied either continuously or intermittently. However, it is preferred to introduce either electromagnetic energy or thermal energy continuously in order to sustain a continuous reaction. Sufficient thermal energy may be available in the form of exothermic heat released from the reaction of halogen with the alkane.

The proportions of halogen and alkane in the feed to the reactor may be varied over a wide range. Preferably the molar ratio of alkane to halogen in the feed is in the range 10:1 to 1:10. Gas hourly space velocities (GHSVs) for the feed may also be varied over a wide range. Suitably the GHSVs may be in the range from 1 to 10,000 preferably 30 to 2000. The units for GHSV are cc(total gaseous reactants)/hour/gram (inert material).

In order to achieve high selectivities to alkyl mono-halides the reaction temperature must be controlled. In the absence of electromagnetic radiation the temperature must be controlled at a value greater than the thermal initiation temperature. The reaction temperature must be selected with reference to the reactants. In the case of the reaction of methane with chlorine for example the reaction temperature in the absence of electromagnetic radiation may suitably be greater than about 180°C, preferably in the range 180 to 280°C. In the case of the reaction of ethane with chlorine in the absence of electromagnetic radiation lower temperatures may be employed, for example greater than about 70°C. Using electromagnetic radiation the process can be operated at temperatures below 180°C.

The process may be operated at subatmospheric, atmospheric or superatmospheric pressures. Operation at atmospheric or superatmospheric pressure is preferred.

The reaction may be carried out batchwise or

continuously, preferably continuously.

It is preferred to recycle unreacted alkane and halogen to the reaction.

It is preferred to utilise the process of the invention to produce methyl chloride or bromide by reacting methane with chlorine or bromine respectively.

The invention will now be illustrated by reference to the following Examples.

Example 1

A mixture of methane and chlorine (mole ratio 1:1) was passed over alumina in a continuous flow reactor (GHSV 1780 cc of gaseous reactants/hour/gram of alumina) which was heated by means of an electric furnace. All light was excluded from the gaseous reaction mixture whilst in the feed lines, the heated zone where the temperature of the alumina bed was 270°C, and the product lines. The product stream was analysed by gas chromatography.

The composition of the product stream, excluding unreacted reactants and hydrogen chloride was methyl chloride (91% v/v) and methylene chloride (9% v/v) and the methane conversion was 36%.

Comparison Test

Example 1 was repeated except that the temperature of the alumina bed was 66°C.

The composition of the product gas stream was essentially the same as the reaction feed stream with less than 0.1% conversion of methane to chlorinated products.

This Example is presented for comparison only and demonstrates that no reaction is obtained at lower temperatures in the absence of light.

Example 2

A mixture of methane and chlorine (mole ratio 1:2) was passed over glass wool in a continuous flow reactor (total gas flow 120 cc/min) which was heated by means of an electric furnace. All light was excluded from the gaseous reaction mixture whilst in the feed lines, the heated zone where the temperature of the glass wool was 234°C, and the product lines. The product gas stream was analysed by gas chromatography.

The composition of the product stream, excluding unreacted reactants and hydrogen chloride was methyl chloride (95% v/v) and methylene chloride (5% v/v) and the methane conversion was 15%.

Example 3

A mixture of methane and chlorine (mole ratio 1:4) was passed through an empty Pyrex (RTM) continuous flow reactor (total gas flow 62 cc/min) which was heated by means of an electric furnace. All light was excluded from the gaseous reaction mixture in the feed line and the heated zone where the temperature of the furnace was 184°C. Light was not excluded from the product line or from that part of the reactor where the reaction mixture left the heated zone. The product gas stream was analysed by gas chromatography.

The composition of the product stream, excluding unreacted reactants and hydrogen chloride was methyl chloride (86% v/v) and methylene chloride (14% v/v) and the methane conversion was 50%.

Example 4

A mixture of methane and chlorine (mole ratio 1:1) was passed over alumina in a continuous flow reactor (GHSV 211 cc of gaseous reactants/hour/gram of alumina) which was heated by a Pyrex (RTM) glass electric furnace. No precautions were taken to exclude light from the gaseous reaction mixture whilst in the feed lines, the heated zone where the temperature of the alumina bed was 200°C, and the product lines. The product gas stream was analysed by gas chromatography.

The composition of the product gas stream, excluding unreacted reactants and hydrogen chloride was methyl chloride (82% v/v) and methylene chloride (18% v/v) and the methane conversion was 52%.

Example 5

A mixture of ethane and chlorine (mole ratio 1:1) was passed over alumina in a continuous flow reactor (GHSV 150 cc of gaseous reactants/hour/gram of alumina) which was heated by means of an electric furnace. All light was excluded from the gaseous reaction mixture whilst in the feed lines, the heated zone where the temperature of the alumina bed was 185°C, and the product lines. The product gas stream was analysed by gas chromatography.

The composition of the product stream, excluding unreacted reactants and hydrogen chloride was ethyl chloride (88% v/v) and 1,2-dichloroethane (12% v/v) and the conversion of ethane was 65%.

CLAIMS

1. A process for the selective production of an alkyl monohalide wherein the alkyl substituent is methyl or ethyl which process comprises reacting a halogen with an alkane which is methane or ethane, in the absence of a catalyst and at a temperature below 300°C, provided that in the absence of electromagnetic radiation the temperature is greater than the thermal initiation temperature.

2. A process according to claim 1 wherein the halogen is chlorine, the alkane is methane and the product is methyl chloride.

3. A process according to either claim 1 or claim 2 wherein the halogen is reacted with the alkane in the presence of a chemically inert material.

4. A process according to claim 3 wherein the inert material is either glass wool, alumina, silica, clay or porcelain.

5. A process according to any one of the previous claims wherein the reaction is initiated by thermal energy, electromagnetic radiation energy, chemical energy or a combination thereof.

6. A process according to claim 5 wherein further quantities of initiation energy are supplied during the reaction.

7. A process according to claim 6 wherein electromagnetic radiation energy or thermal energy is supplied continuously to the reaction.

8. A process according to any one of the preceding claims wherein the alkane is methane, the

halogen is chlorine and the reaction temperature in the absence of electromagnetic radiation is greater than about 180°C.

9. A process according to claim 8 wherein the reaction temperature is in the range 180 to 280°C.

10. A process according to any one of claims 1 to 7 wherein the alkane is ethane, the halogen is chlorine and the reaction temperature in the absence of electromagnetic radiation is greater than about 70°C.

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